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(54) Improving the quality of coated paper

(57) There is disclosed a method for improving the ease of application of a final inorganic pigment-containing coating to a cellulosic sheet material which has been coated with at least one preliminary inorganic pigment-containing coating. The method comprises incorporating into the preliminary coating or into at least one of the preliminary coatings, up to 2% by weight, based upon the weight of the inorganic pigment, of a sizing reagent, such as an alkyl ketene dimer. A composition for use in the method is also disclosed.

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Description

This invention relates to the improvement of the quality of a coated cellulosic sheet material which is prepared by applying, to a cellulosic sheet material base, two or more mineral pigment-containing coating compositions.

If a high quality printed image is to be applied to a cellulosic sheet material such as paper or cardboard it is generally necessary to apply to the surface at least one coating composition containing one or more mineral pigments such as kaolin clay, calcium carbonate, calcium sulphate, titanium dioxide, barium sulphate, satin white and the like. The application of such a coating composition improves the smoothness, gloss, whiteness and opacity of the surface to which the printed image is to be applied. In many cases, in order to obtain a final coated surface of the desired quality, it is necessary to apply two or more layers of pigment-containing coating compositions.

Generally, in order to receive the maximum return from capital invested in paper coating machinery, it is desirable to run the coating machine at the highest practicable web speed. Also, since the coating compositions consist of pigment, adhesives, and possibly other solid ingredients in suspension in water, it is necessary to remove the water content of the composition by thermal evaporation in order to dry the coating. In order to minimise the consumption of energy for thermal evaporation it is desirable to operate with coating compositions having the highest possible solids concentrations. However, it is found that when a final coating composition of relatively high solids concentration is applied to a base sheet of relatively high water absorbency, there is a tendency, when a doctor blade is used to remove excess coating composition and smooth the coating, for this final coating to be marred by scratches and other defects.

An object of this invention is to provide a method in which two or more coatings are applied to a cellulosic sheet base, and in which it is possible to achieve a final surface of good quality at a relatively high web speed in the coating machine and with a final coating composition of high solids concentration.

It is well known to use water-repellant chemical reagents in the production of cellulosic sheet products. The absorption of water into the sheet product may be controlled by a process known as "sizing". There are generally two main types of sizing process, internal sizing and surface sizing. In internal sizing a water-repellant reagent is mixed with the pulp of cellulosic fibres prior to the formation of the sheet. In surface sizing, the reagent, which is usually starch in this case, is applied to a web of ready formed sheet material, by passing the web through a coating trough known as a "size press". Generally, in surface sizing, both sides of the web are coated with a film of the reagent.

The most commonly used sizing reagent for internal sizing is rosin which is precipitated in a suspension of cellulosic fibres by the addition of aluminium sulphate. However, this treatment reduces the pH of the suspension of fibres to about 4-6 which renders it unsuitable for use when an alkaline filler, such as calcium carbonate, is incorporated into the suspension.

In order to size a cellulosic sheet material containing an alkaline filler, sizing agents have been developed which confer water-repellant properties to the cellulosic fibres at neutral or alkaline pH values. Examples of these sizing agents include those of the alkyl ketene dimer type which are described in United States Patent Specification No. 2627477, and those of the alkenyl succinic anhydride type which are described in United States Patent Specification No. 3102064.

The present invention provides a method for improving the ease of application of a final inorganic pigment-containing coating to a cellulosic sheet material which has been coated with at least one preliminary inorganic pigment-containing coating, which method comprises incorporating into the preliminary coating or into at least one of the preliminary coatings, up to 2% by weight, based upon the weight of the inorganic pigment, of a sizing reagent.

The present invention also provides a method of coating a cellulosic sheet material, which method comprises coating the cellulosic sheet material with at least one preliminary inorganic pigment-containing coating and then with a final inorganic pigment-containing coating, wherein there is present in the preliminary coating or in at least one of the preliminary coatings, up to 2% by weight, based upon the weight of the inorganic pigment, of a sizing reagent.

The present invention further provides a composition for forming a preliminary inorganic pigment-containing coating on a cellulosic sheet material, the composition comprising an inorganic pigment and up to 2% by weight, based on the weight of the inorganic pigment, of a sizing reagent.

The sizing reagent is conveniently an alkyl ketene dimer of the type which is used as an internal size for paper under alkaline or neutral conditions. Such an alkyl ketene dimer has the general formula:-

$$\begin{array}{l} R-CH-C=O \\ \quad\;\;\, | \quad\;\; | \\ O=C\;-CH-R \end{array}$$

where R is an alkyl group having from 8 to 20 carbon atoms.

The sizing reagent may also be, for example, a styrene-maleic anhydride copolymer, an alkenyl succinic anhydride or an anionic polyurethane.

The inorganic pigment in both the preliminary and the final coating compositions may be chosen from the group consisting of kaolin clay, calcium carbonate, titanium dioxide, calcium sulphate, barium sulphate and satin white. In addition to the inorganic pigment, both the final and the preliminary coating compositions will also include from 4% to 20% by weight, based on the weight of the inorganic pigment, of an adhesive for the pigment which is generally chosen from the group consisting of starches, proteinaceous adhesives such as casein, and latices of, for example, styrene butadiene rubber or an acrylic polymer. The coating compositions will also generally contain from 0.02% to 1% by weight, based on the weight of the pigment, of a dispersing agent for the inorganic pigment.

The amount of the sizing reagent used in the preliminary coating composition is preferably in the range from 0.01% to 0.30% by weight, based on the weight of the inorganic pigment.

The invention will now be illustrated by the following Examples, wherein reference is made to Figures 1 to 4 of the accompanying drawings.

EXAMPLE 1

Three coating compositions were prepared for use in providing the first of two coatings applied to a base paper to form a double coated paper. Each composition was prepared according to the general recipe:-

Ingredient	Parts by Weight
Calcium carbonate pigment	100
Adhesive	15

The calcium carbonate pigment was a comminuted natural marble which had a particle size distribution such that 60% by weight consisted of particles having an equivalent spherical diameter smaller than 2μm.

The adhesive used in each of the three compositions was:

A 15 parts by weight of starch
B 12 parts by weight of starch and 3 parts by weight of latex solids
C 10 parts by weight of starch and 5 parts by weight of latex solids

The starch was an oxidised corn starch which is marketed by Cerestar under the trade name "AMISOL 05591". The latex contained 50% by weight of styrene butadiene rubber polymer and is marketed by The Dow Chemical Company under the trade name "DOW 950". The amounts of latex used in the recipes given above are expressed in terms of the weight of dry polymer solids.

Each composition was divided into two portions, 1 and 2. To Portion 1 there was added 0.25 parts by weight, on a dry weight basis, per hundred parts by weight of calcium carbonate pigment, of a weakly cationic alkyl ketene dimer which is marketed by the Hercules Corporation under the trade name "AQUAPEL C519". No alkyl ketene dimer was added to Portion 2.

Each composition was applied to an unsized, absorbent, woodfree base paper by means of a laboratory paper coating machine of the type described in British Patent Specification No. 1032536 at a paper speed of $400 m.min^{-1}$. In each case the coating was dried by blowing air over it for 2 minutes.

Each sample of paper coated with a first coating composition was then coated by means of a laboratory bench blade coating apparatus with a second composition having the general formula:-

Ingredient	Parts by Weight
Fine calcium carbonate pigment	100
Latex adhesive	12
Sodium carboxymethyl cellulose	1

The fine calcium carbonate pigment was a comminuted natural marble having a particle size distribution such that 95% by weight consisted of particles having an equivalent spherical diameter smaller than 2μm. The latex adhesive was the same as that used for the first coat, and the sodium carboxymethyl cellulose was that marketed by Metsa Serla

under the trade name "FINNFIX 5". Each sample of paper coated with each of the six different first coating compositions was divided into a number of portions and the blade pressure in the coating apparatus was varied to give a series of different weights per unit area of the second composition in the range from 8 to 20g.m^{-2}.

The coating apparatus was provided with a device which monitored the rate of drying of the second coating composition by measuring the intensity of light reflected from the surface of the coated paper. The coating immediately after passing beneath the blade was uniformly wet and was therefore highly reflective to light. However, as the coating dried it became duller in appearance. An adjustable light source and a detector were mounted above the coating apparatus to give an incident light beam and a measured beam both at an angle of 75° to the normal to the paper. The signal from the detector was applied by way of a voltage measurement interface to an input of a personal computer. The computer was capable of recording up to 15,000 measurements of light intensity per second, so, in order to provide 150 data points per second, the average of 100 such measurements was calculated to give each data point.

For each sample of paper to be coated, measurements of reflected light intensity were made for about 2 seconds on dry paper. The coating apparatus was then started and a drying curve of light intensity against time was recorded by the computer. A typical drying curve takes the form of an initial drop in light intensity to near zero as the blade passes beneath the source and detector, followed by a rapid increase in intensity as the wet coating film is exposed. The intensity will then begin to decrease as the coating dries and will eventually become constant to give a measure of the reflectance of light from the dry coated paper. For each sample of paper, the rate of drying was expressed as a drying parameter, δ. The value of δ was determined precisely by plotting the rate of change of light intensity with time and reading as δ the time interval between the maximum positive gradient of the light intensity/time curve, when the wet coating is first sensed, and the greatest negative gradient of this curve, when the rate of change of light intensity is at a maximum and the coating is in a partially dried state.

For each of the six first coating compositions a graph was plotted of drying parameter, δ, against coat weight and the results are shown in Figures 1-3. Figure 1 gives the results for first coating compositions A1 and A2, with and without the alkyl ketene dimer, respectively; Figure 2 gives the results for first coating compositions B1 and B2 and Figure 3 gives the results for first coating compositions C1 and C2.

It will be noted that in every case the drying parameter, δ, and hence the drying time, increases with coat weight, but that, for each adhesive system used in the first coating composition, the second coat dries more slowly when the alkyl ketene dimer is added to the first coating composition.

EXAMPLE 2

Batches of an absorbent woodfree base paper of weight 83g.m^{-2} were precoated with four different first coating compositions, each of which was prepared to the general recipe:-

Ingredient	Parts by weight
Calcium carbonate pigment	100
Oxidised starch adhesive	18
Sodium hydroxide	to pH 8.5
Alkyl ketene dimer	see below
Water	to 62% solids

The calcium carbonate pigment was the same as that used in the first coating composition in Example 1.

The amounts of the alkyl ketene dimer in the four compositions were, respectively, 0, 0.02, 0.05 and 0.1 parts by weight of active alkyl ketene dimer per 100 parts by weight of the pigment. The alkyl ketene dimer was the same as that used in Example 1. The alkyl ketene dimer, when used, was added into the composition after the starch adhesive at a temperature below 40°C.

The first coating composition was applied to the base paper in each case by means of a pilot-scale paper coating machine fitted with a roll applicator and a doctor blade at a web speed of 600m.min^{-1} and a blade angle of 49°. The blade pressure was adjusted to give a coat weight of 10g.m^{-2}. In order to minimise curl of the paper during the second coating step, a first coating composition was also applied to the reverse side of the paper web at a coat weight of 8.5g.m^{-2}.

After the first coating composition had been applied to each batch of paper, the surface of the coated paper was calendered by passing it through two nips of a supercalender at a line pressure of 50kN.m^{-1} at 60°C and at a speed of 600m.min^{-1}.

Each sample of paper coated with a first coating composition was then coated with a second coating composition having the general formula:-

Ingredient	Parts by Weight
Fine calcium carbonate pigment	100
Styrene butadiene latex	12
Sodium carboxymethyl cellulose	1
Optical brightening agent	0.5

The fine calcium carbonate pigment, the latex and the sodium carboxymethyl cellulose were the same as those used in Example 1.

The second coat was applied to each batch of precoated paper by means of a pilot-scale paper coating machine fitted with a roll applicator and a doctor blade. The blade pressure was kept constant at a suitable value which would give a coat weight of the second coating of $9g.m^{-2}$.

The runnability, or resistance to scratching, of the second coat was investigated by the following procedure:-

A second coat was applied first to a batch of base paper which had been precoated with a first coating composition containing no alkyl ketene dimer. The second coating composition was applied at a web speed of $300m.min^{-1}$ at the highest solids concentration which would permit the application of a coat weight of $9g.m^{-2}$. The web speed was then increased until scratching was observed at the blade. When scratching was observed, the base paper was changed to a base paper which had been precoated with a first coating composition which contained some alkyl ketene dimer, and a second coat was applied to this paper keeping the second coating composition and the coating machine settings unchanged. If an improvement in the resistance to scratching was observed, the web speed was increased until scratching was observed, or until a web speed of $800m.min^{-1}$ was reached.

The second coating composition was then diluted with water by about 1-2% by weight of solids and coated on to the base paper which had been precoated with a first coating containing no alkyl ketene dimer. The procedure was then repeated until no scratching could be detected during the application of a second coat to the base paper which had been precoated with the first coating which contained no alkyl ketene dimer.

The whole procedure was then repeated using the base papers which had been precoated with the first coating compositions which contained different amounts of the alkyl ketene dimer.

The results are set forth in Table 1 below:

Table 1

Amount of alkyl ketene dimer in first coat (pph)	% by weight solids in second coat	web speed ($m.min^{-1}$)	Observations
0	69.0	300	Frequent scratching
0	67.4	300	Slight scratching
0	65.7	300	Slight scratching
0	63.9	300	No scratching
0.02	68.4	300	Slight scratching
0.02	66.8	300	No scratching
0.02	66.8	800	No scratching
0.05	66.6	800	No scratching
0.10	68.6	300	No scratching
0.10	68.6	600	Scratching reappeared
0.10	66.9	600	No scratching
Note:- "pph" means parts by weight per 100 parts by weight of pigment.			

These results show that scratching was most pronounced when a second coating composition was being applied at a high solids concentration (68-69% by weight) on to a base paper which had been precoated with a first coating composition containing no alkyl ketene dimer. The inclusion of only 0.02 parts by weight of alkyl ketene dimer into the first coating composition was sufficient to reduce scratching markedly when a second coating composition was applied at a solids concentration of 68-69% by weight. When a first coating containing 0.1 parts by weight of alkyl ketene dimer was applied, scratching during the application of a second coating composition was completely eliminated under the same conditions.

EXAMPLE 3

Batches of an absorbent woodfree base paper of weight $94g.m^{-2}$ were precoated with three different first coating compositions having the following recipes:-

1. 100 parts by weight calcium carbonate pigment A; 15 parts by weight oxidised corn starch.
2. 100 parts by weight calcium carbonate pigment B; 15 parts by weight oxidised corn starch; 0.6 part by weight sodium salt of styrene-maleic acid copolymer.
3. 100 parts by weight calcium carbonate pigment A; 15 parts by weight oxidised corn starch; 0.25 part by weight alkenyl succinic anhydride.

Calcium carbonate pigment A was the same as that used in the first coating composition in Example 1.

Calcium carbonate pigment B was a natural marble which was comminuted to a similar particle size distribution as that of calcium carbonate pigment A, but in an aqueous suspension of lower solids concentration and in the absence of a dispersing agent.

The oxidised corn starch was the same as that used in Example 1.

The sodium salt of the styrene-maleic acid copolymer was supplied by Atochem under the trade name "SMA 3000".

The alkenyl succinic anhydride was supplied by Claymore Chemicals Limited under the trade name "CLAYSIZE PR4".

In each case the oxidised corn starch was added to the coating composition in the form of a 30% by weight solution which was cooked at 90°C for 20 minutes before addition.

In the case of compositions 1 and 3, the cooked starch solution was added to an aqueous suspension containing 78% by weight of calcium carbonate pigment A and a sodium polyacrylate dispersing agent. In the case of composition 3, the alkenyl succinic anhydride was mixed in to the composition immediately before coating.

Composition 2 was prepared by mixing 1333g of a cake containing 75% by weight of the dry calcium carbonate pigment B with 6g of the sodium salt of the styrene-maleic acid copolymer. A deflocculated suspension of the calcium carbonate pigment at a solids concentration of 74.4% by weight was obtained.

Each first coating composition was applied to the base paper by means of the laboratory paper coating machine described in Example 1 at a paper speed of $400m.min^{-1}$ and a blade angle of 35°. The blade angle was adjusted, if necessary, to give a coat weight of $8.0 \pm 0.5g.m^{-2}$ for each first composition. The coatings were dried by infrared heating for 25 seconds with a current of hot air followed by 25 seconds during which cold air was blown over the coated surface.

Each sample of paper coated with a first coating composition was then coated by means of the laboratory bench blade coating apparatus with a second coating composition having the general formula:-

Ingredient	Parts by Weight
Fine calcium carbonate pigment	100
Latex adhesive	12
Sodium carboxymethyl cellulose	1

The fine calcium carbonate pigment, the latex adhesive and the sodium carboxymethyl cellulose were the same as those used in Example 1. Each sample of paper coated with each of the three different first coating compositions was divided into a number of portions and the blade pressure in the bench coating apparatus was varied to give a series of different weights per unit area of the second coating composition in the range from 8 to $20g.m^{-2}$. For each first coating composition a graph was drawn of drying parameter, δ, against coat weight, and the results are shown in Figure 4. It will be seen that for the control first coating composition 1 the drying parameter remains virtually constant with second composition coat weight, while in the case of first compositions 2 and 3, in accordance with the invention, the drying

parameter increases steeply with second composition coat weight, indicating that the second coat dries more slowly when a sizing reagent is added to the first composition.

EXAMPLE 4

Batches of an absorbent woodfree base paper of weight $83g.m^{-2}$ were precoated with three different first coating compositions, each of which was prepared according to the general recipe:-

Ingredient	Parts by weight
Calcium carbonate pigment	100
Oxidised starch adhesive	18
Sodium hydroxide	to pH 8.5
Sizing reagent	see below
Water	to 62% solids

The calcium carbonate pigment was the same as that used in the first coating composition in Example 1.

The sizing reagent was an anionic polyurethane marketed by Eka Nobel under the trade name "CYCLOPAL A" and the amounts used in the three compositions were, respectively, 0, 0.1 and 0.2 parts by weight of active anionic polyurethane per 100 parts by weight of the pigment. The anionic polyurethane was added into the composition before the starch adhesive.

The first coating composition was applied to the base paper in each case by means of a pilot-scale paper coating machine fitted with a roll applicator and a doctor blade at a web speed of $600m.min^{-1}$ and a blade angle of 49°. The blade pressure was adjusted to give a coat weight of $10g.m^{-2}$. It was not necessary in this case to apply a first coating to the reverse side of the paper web, as the paper coated on one side only was found, after calendering, to have sufficient resistance to curling.

After the first coating had been applied to each batch of paper, the surface of the coated paper was calendered by passing it through two nips of a supercalender at a line pressure of $50kN.m^{-1}$ at 60°C and at a speed of $600m.min^{-1}$.

Each sample of paper coated with a first coating composition was then coated with a second coating composition having the general formula:-

Ingredient	Parts by Weight
Fine calcium carbonate pigment	100
Styrene butadiene latex	12
Sodium carboxymethyl cellulose	1
Optical brightening agent	0.5

The fine calcium carbonate pigment, the latex and the sodium carboxymethyl cellulose were the same as those used in Example 1.

The second coat was applied to each batch of precoated paper by means of a pilot-scale paper coating machine fitted with a roll applicator and a doctor blade. The blade pressure was kept constant at a suitable value which would give a coat weight of the second coating of $9g.m^{-2}$.

The runnability, or resistance to scratching, of the second coating was investigated by the procedure described in Example 2. The results are set forth in Table 2 below:

Table 2

Amount of anionic polyurethane in first coat (pph)	% by weight solids in second coat	web speed (m.min^{-1})	Observations
0	69.2	500	Frequent scratching
0	69.2	1000	Frequent scratching
0	67.2	500	No scratching
0.1	69.0	500	Slight scratching
0.1	69.0	1000	No scratching
0.2	69.1	300	No scratching
0.2	69.1	1000	No scratching

These results show that the inclusion of the anionic polyurethane into the first coating composition at a level of 0.1 part by weight per 100 parts by weight of pigment greatly reduces scratching when the second coating composition is applied at a solids concentration of about 69% by weight.

Claims

1. A method for improving the ease of application of a final inorganic pigment-containing coating to a cellulosic sheet material which has been coated with at least one preliminary inorganic pigment-containing coating, which method comprises incorporating into the preliminary coating or into at least one of the preliminary coatings, up to 2% by weight, based upon the weight of the inorganic pigment, of a sizing reagent.

2. A method of coating a cellulosic sheet material, which method comprises coating the cellulosic sheet material with at least one preliminary inorganic pigment-containing coating and then with a final inorganic pigment-containing coating, wherein there is present in the preliminary coating or in at least one of the preliminary coatings, up to 2% by weight, based upon the weight of the inorganic pigment, of a sizing reagent.

3. A method according to claim 1 or 2, wherein the inorganic pigment is kaolin clay, calcium carbonate, titanium dioxide, calcium sulphate, barium sulphate or satin white.

4. A method according to any of claims 1 to 3, wherein the sizing reagent is an alkyl ketene dimer.

5. A method according to any of claims 1 to 4, wherein the sizing reagent is present in an amount of from 0.01 to 0.30% by weight, based on the weight of the inorganic pigment.

6. A method according to any of claims 1 to 5, wherein the preliminary and/or final compositions additionally contain an adhesive.

7. A method according to claim 6, wherein the adhesive is a starch, a proteinaceous adhesive or a polymer latex.

8. A method according to claim 6 or 7, wherein the adhesive is present in an amount of from 4 to 20% by weight, based on the weight of the inorganic pigment.

9. A method according to any of claims 1 to 8, wherein the preliminary and/or final compositions additionally contain a dispersing agent.

10. A method according to claim 9, wherein the dispersing agent is present in an amount of from 0.02 to 1% by weight, based on the weight of the inorganic pigment.

11. A composition for forming a preliminary inorganic pigment-containing coating on a cellulosic sheet material, the composition comprising an inorganic pigment and up to 2% by weight, based on the weight of the inorganic pigment, of a sizing reagent.

12. A composition according to claim 11, wherein the inorganic pigment is kaolin clay, calcium carbonate, titanium dioxide, calcium sulphate, barium sulphate or satin white.

13. A composition according to any of claims 11 to 12, wherein the sizing reagent is an alkyl ketene dimer.

14. A composition according to any of claims 11 to 13, wherein the sizing reagent is present in an amount of from 0.01 to 0.30% by weight, based on the weight of the inorganic pigment.

15. A composition according to any of claims 11 to 14, wherein the preliminary and/or final compositions additionally contain an adhesive.

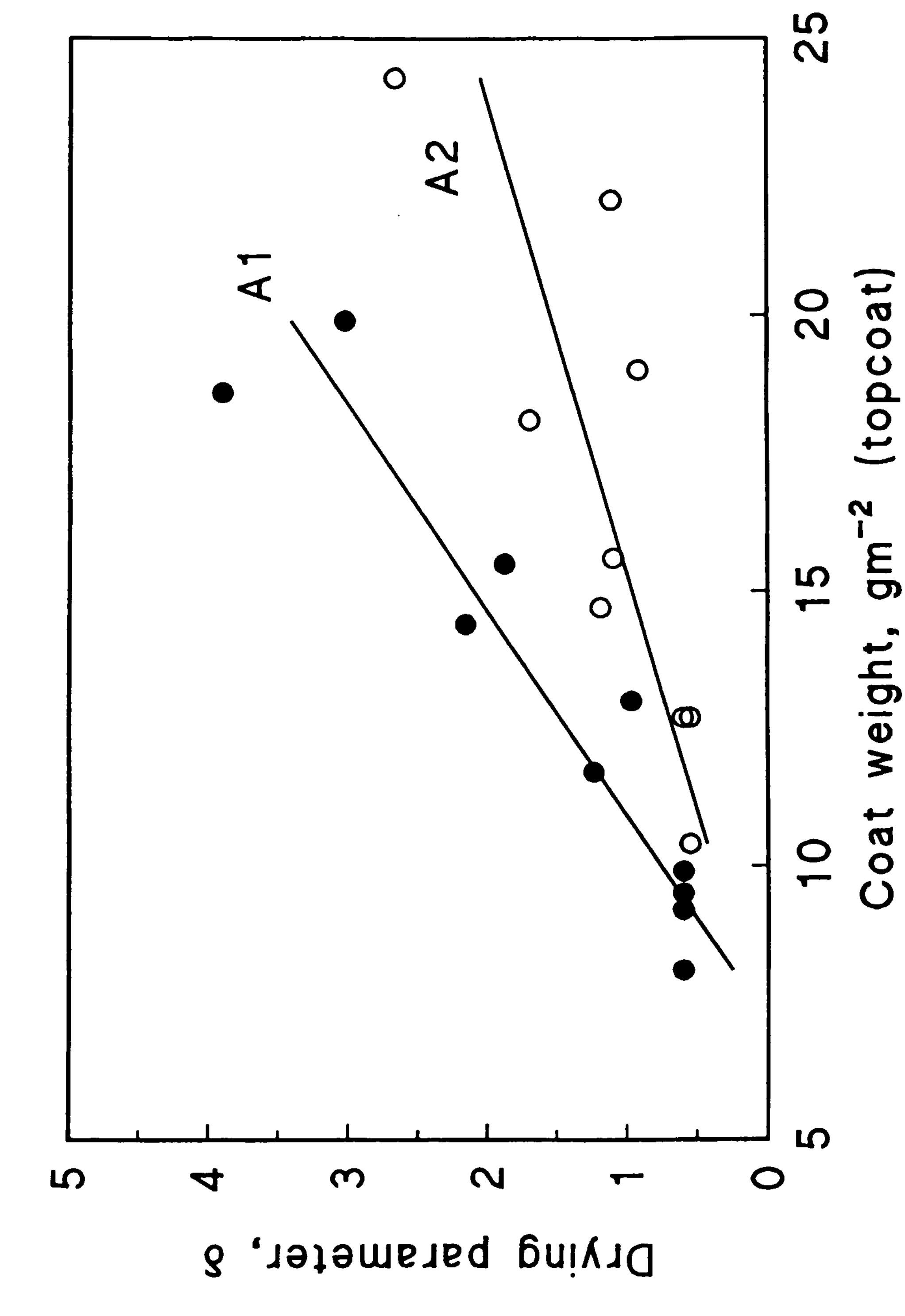
16. A composition according to claim 15, wherein the adhesive is a starch, a proteinaceous adhesive or a polymer latex.

17. A composition according to claim 15 or 16, wherein the adhesive is present in an amount of from 4 to 20% by weight, based on the weight of the inorganic pigment.

18. A composition according to any of claims 11 to 17, wherein the composition additionally contains a dispersing agent.

19. A composition according to claim 18, wherein the dispersing agent is present in an amount of from 0.02 to 1% by weight, based on the weight of the inorganic pigment.

FIG. 1.



Drying parameter, δ
Coat weight, gm⁻² (topcoat)
A1
A2
0
1
2
3
4
5
5
10
15
20
25

FIG. 2.

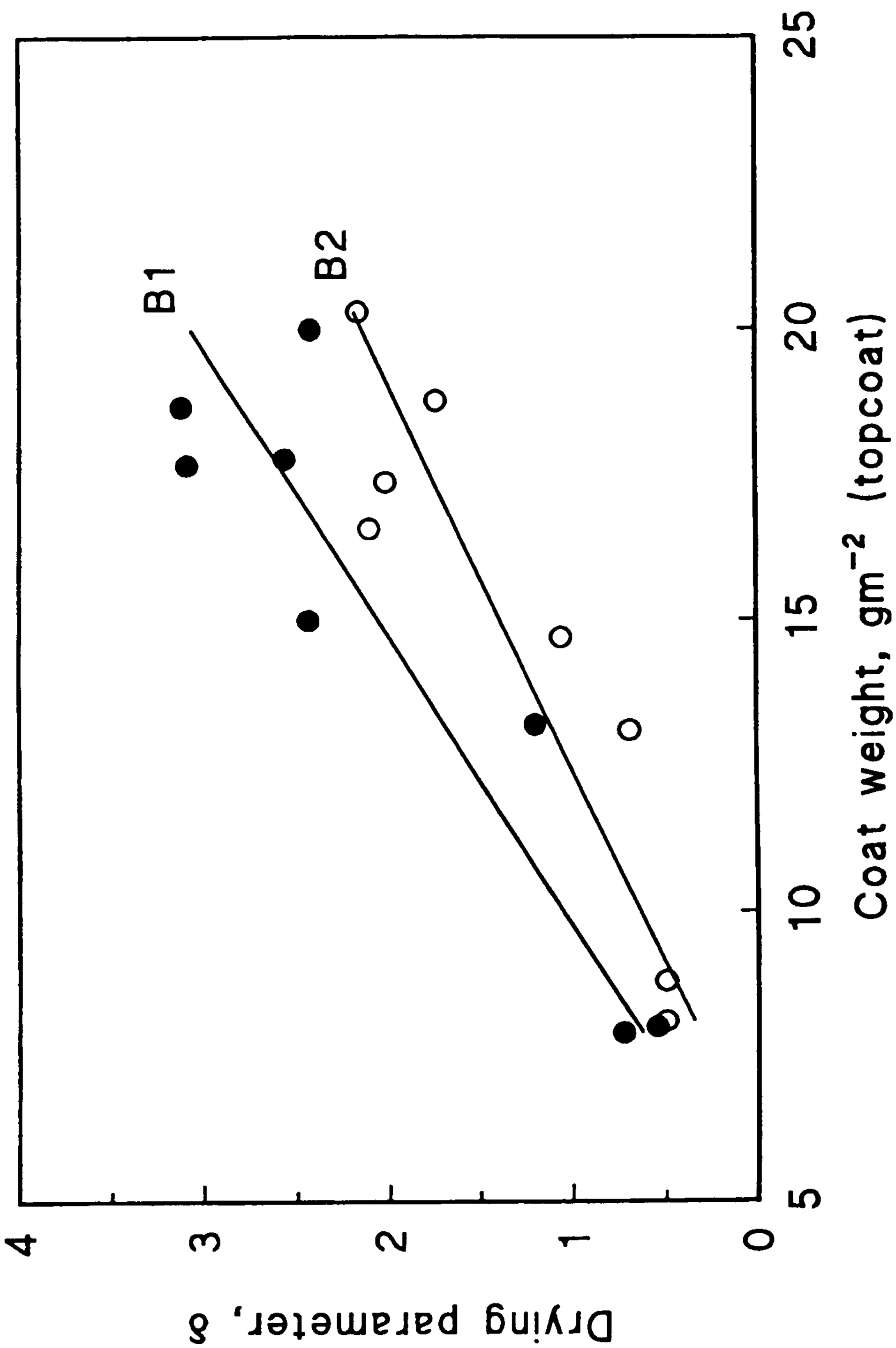

B1
B2
0
1
2
3
4
Drying parameter, δ
5
10
15
20
25
Coat weight, gm^{-2} (topcoat)

FIG. 3.

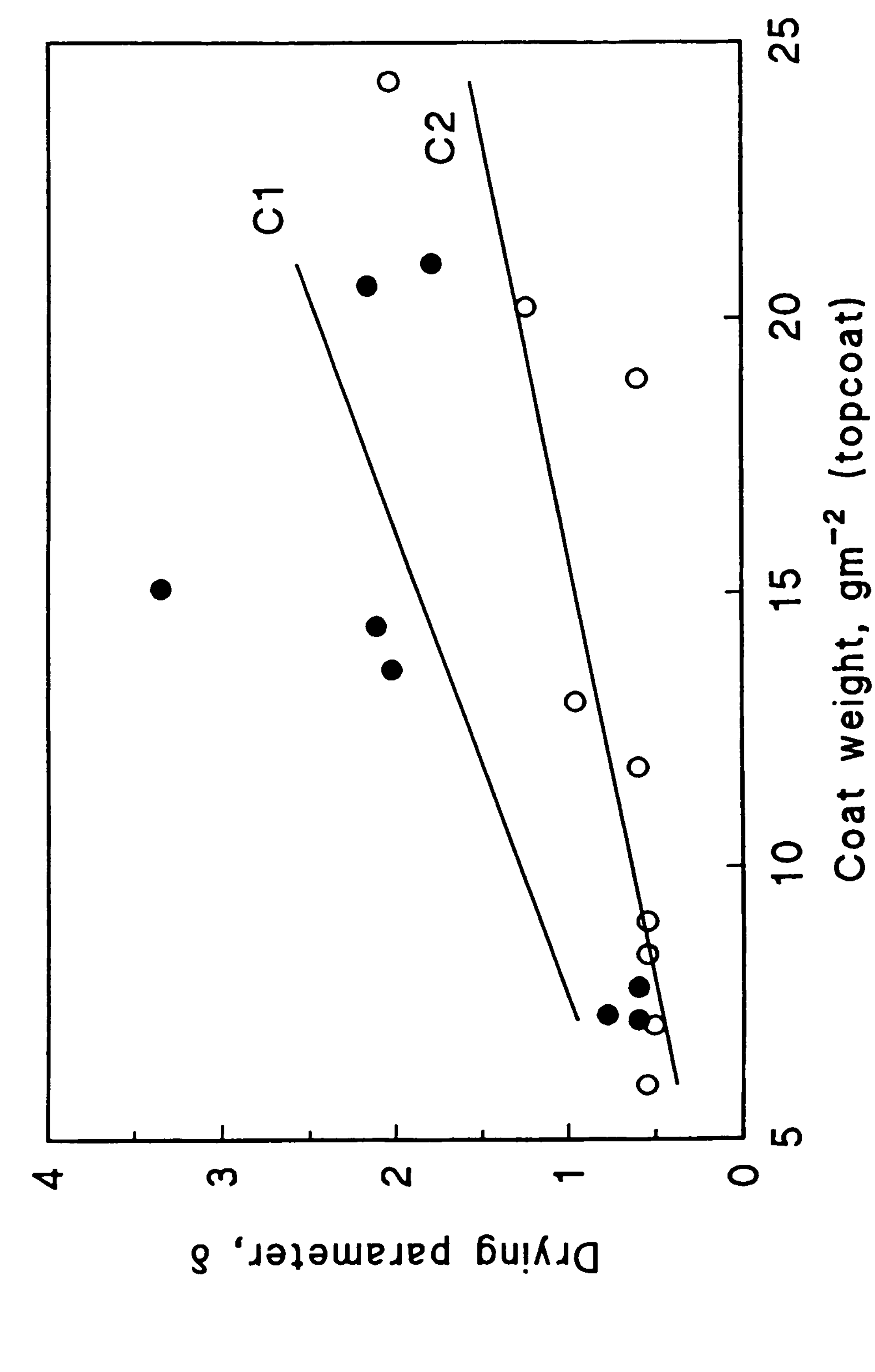
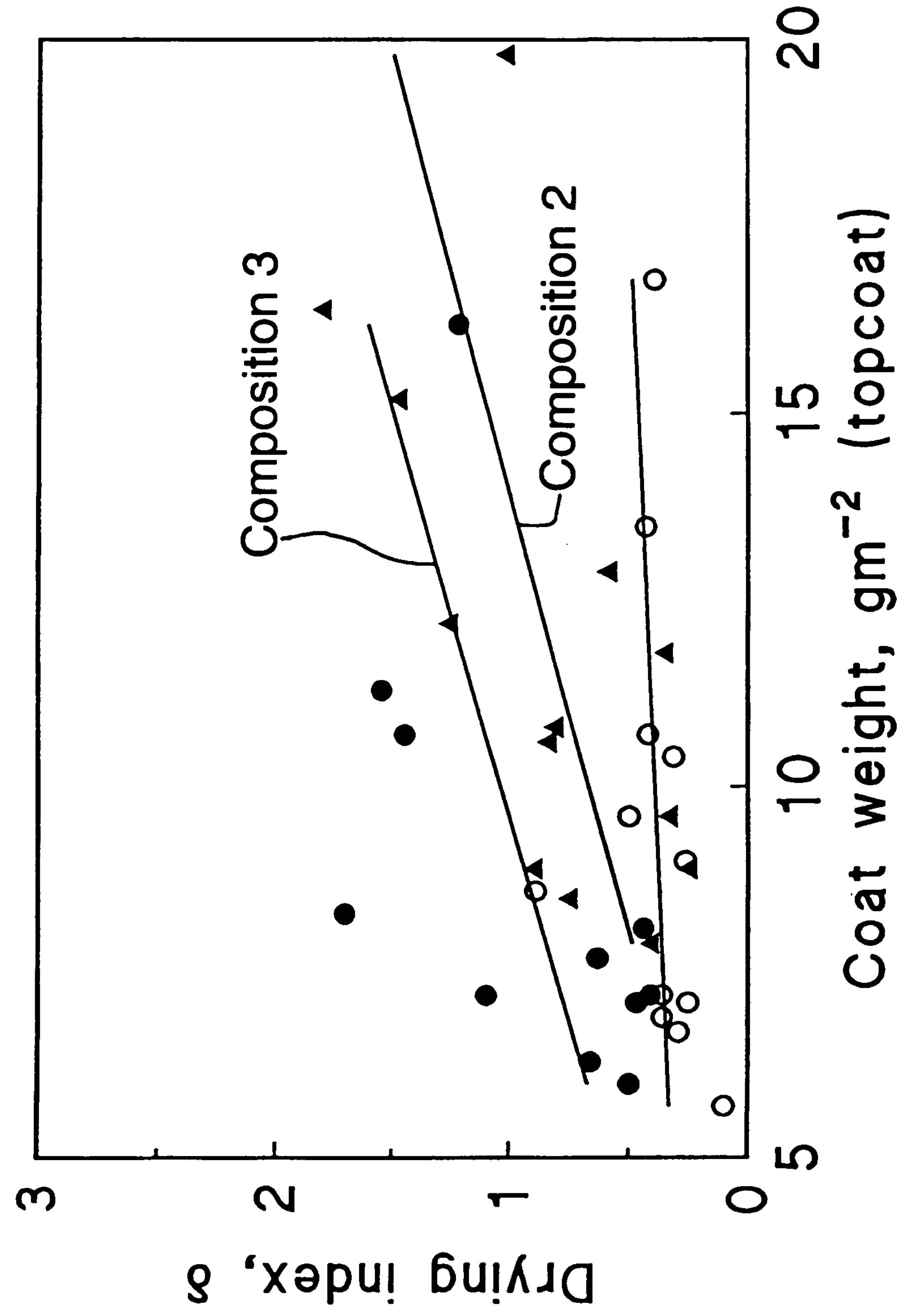

C1
C2
Coat weight, gm^{-2} (topcoat)
Drying parameter, δ
5
10
15
20
25
0
1
2
3
4

FIG. 4.


Composition 3
Composition 2
Drying index, δ
0
1
2
3
5
10
15
20
Coat weight, gm^{-2} (topcoat)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 6964

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DATABASE WPI Section Ch, Week 9409 Derwent Publications Ltd., London, GB; Class A82, AN 94-072445 & JP-A-06 025 999 (KANZAKI PAPER MFG CO LTD) , 1 February 1994 * abstract * ---	1,2,6, 11,15	D21H19/44 D21H19/82 //D21H21:16
X	US-A-4 962 072 (COOPER JOHN B ET AL) 9 October 1990 * column 1, line 37 - column 6, line 32; examples 1-9 * ---	1,3-9, 11-18	
X	EP-A-0 495 591 (JUJO PAPER CO LTD) 22 July 1992 * page 5, line 22-49; claim 1; examples 1-5 * ---	1,3,4,6, 7,9, 11-13, 15,16,18	
A	EP-A-0 487 497 (PATRIA PAPIER & ZELLSTOFF) 27 May 1992 * the whole document * -----	1-3,6,7, 9,11,12, 15,16,18	TECHNICAL FIELDS SEARCHED (Int.Cl.6) D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	11 January 1996	Nestby, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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